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Mendeleev Commun., 2018, **28**, 245–247

Mendeleev Communications

Synthesis and crystal structure of a new hybrid methylammonium iodocuprate

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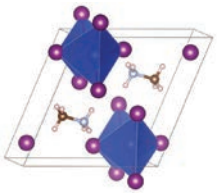
DOI: 10.1016/j.mencom.2018.05.005

The new hybrid organic-inorganic compound $(MeNH_3)Cu_2I_3$ was synthesized using two independent techniques: mechanosynthesis and crystallization from acetonitrile. Its crystal structure was determined by single crystal X-ray diffraction.



Recently, hybrid organic-inorganic compounds became the materials of extremely intense research. While hybrid lead halide perovskites revolutionized the photovoltaics due to their outstanding properties, other hybrid compounds based on non-toxic metals also drew attention owing to their structural versatility and combining properties of organic and inorganic units. This gave rise to a bunch of practical functional features such as ferroelectric and ferromagnetic properties, high values of dielectric constants and dielectric anisotropy, high electrical conductivity, photoluminescence, electroluminescence and nonlinear optical properties.[1–3] Halocuprates(I) have attracted considerable attention due to their potential applications in optics. In particular, iodocuprates(I) exhibit photoluminescence,[4–7] and methylnicotinohydrazide iodocuprate(I) exhibits thermochromic and photochromic properties.[8]

Up to now, iodocuprates with the general formula ACu_2I_3 (where A is a monovalent cation) have been reported for A = rubidium ($RbCu_2I_3$),[9] cesium ($CsCu_2I_3$),[10] trimethylsulfonium $[(Me_3S)Cu_2I_3]$,[11] tetramethylammonium $[(Me_4N)Cu_2I_3]$,[12] tetraethylammonium $[(Et_4N)Cu_2I_3]$[13] and methylpyridinium $[(C_6H_8N)Cu_2I_3]$.[14] These compounds are natural low-dimensional semiconductor systems.[15,16]

Here, we report for the first time a new hybrid organic-inorganic iodocuprate $(MeNH_3)Cu_2I_3$ and refined its crystal structure using synchrotron X-ray radiation. In addition, we evaluated its thermal stability using simultaneous thermal analysis (STA).

Large crystals of $(MeNH_3)Cu_2I_3$ were obtained by crystallization from acetonitrile. $(MeNH_3)I$ (2 mmol) and CuI (4 mmol) were dissolved in acetonitrile (15 ml), which was then vaporized by putting the solution on a rotary evaporator at 50 °C. $(MeNH_3)Cu_2I_3$ precipitated as needle-like crystals (Figure 1), which were then washed with diethyl ether.

We found that a reaction between $(MeNH_3)I$ and CuI proceeds readily, so that $(MeNH_3)Cu_2I_3$ as dispersed powder can be mechanochemically synthesized by the simple grinding of $(MeNH_3)I$ and CuI in a ratio of 1:2 in a mortar for 10 min under an inert atmosphere. The obtained powder consisted solely of the target phase without any traces of the precursors or other impurities with the most intense reflection at 43° corresponding to the (004) plane due to a texturing (Figure 1). The reaction between $(MeNH_3)I$ and CuI in a mortar is similar to that observed for hybrid perovskites where a pure phase of $(MeNH_3)PbI_3$ was obtained by the grinding of $(MeNH_3)I$ and PbI_2.[17,18]

A single crystal of $(MeNH_3)Cu_2I_3$ with a length of ~300 μm for crystal structure refinement was grown by drying a droplet of a saturated solution of $(MeNH_3)I$/CuI with a molar ratio of 1:2, and its crystal structure was then determined for the first time using synchrotron irradiation† (Figure 2). It was also found that

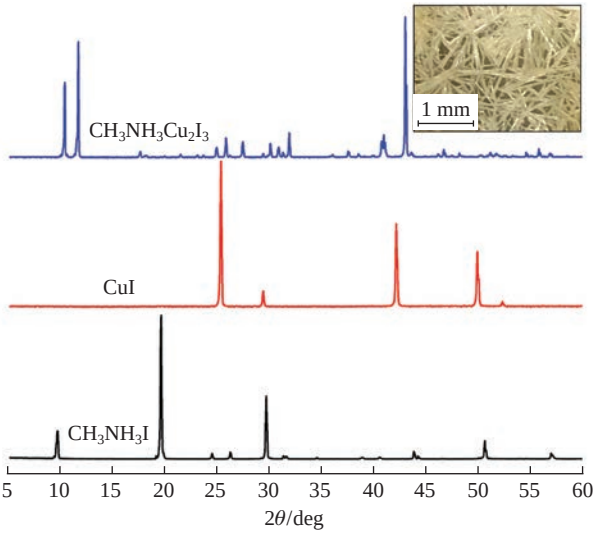


Figure 1 Powder X-ray diffraction data of $(MeNH_3)Cu_2I_3$ and its precursors.

† *Crystal data for* $CH_3NH_3Cu_2I_3$. M = 539.87, monoclinic, space group $P2_1/m$, at 100 K: a = 8.9053(18), b = 5.8982(12) and c = 9.0766(18) Å, β = 112.51(3)°, V = 440.43(18) Å^3, Z = 2, d_{calc} = 4.071 g cm^{-3}, μ = = 34.936 mm^{-1}, $F(000)$ = 472. Total of 4474 reflections were measured and 997 independent reflections (R_{int} = 0.096) were used in a further refinement, which converged to wR_2 = 0.2497 and GOF = 0.976 for all independent reflections [R_1 = 0.1125 was calculated on F for 728 observed reflections with $I > 2\sigma(I)$]. X-ray diffraction data were measured at the 'Belok' beamline (λ = 0.96990 Å) of the Kurchatov Synchrotron

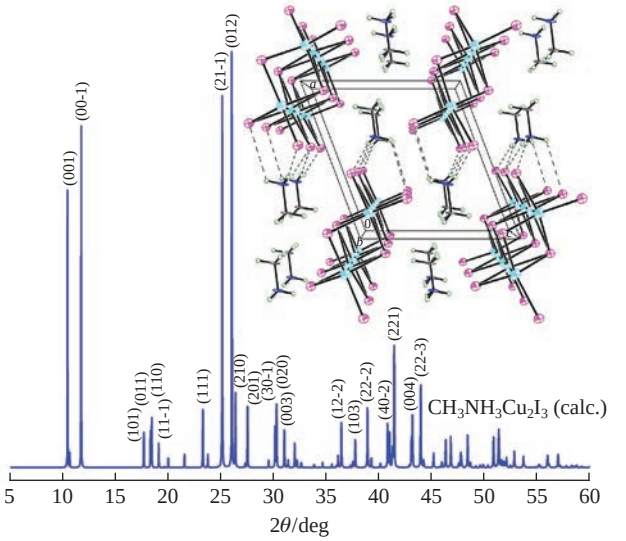


Figure 2 Calculated diffraction pattern of $(MeNH_3)Cu_2I_3$. Inset: the crystal structure of $(MeNH_3)Cu_2I_3$. Selected geometrical parameters (Å and degrees): Cu(1)–I(1) 2.685(2), Cu(1)–I(2) 2.633(2), Cu(1)–I(3) 2.636(2), Cu(1)–I(1A) 2.722(2), Cu(1)···Cu(1A) 2.886(4), Cu(1)···Cu(1B) 3.013(4), I(1)–Cu(1)–I(2) 113.93(8), I(1)–Cu(1)–I(3) 107.62(7), I(2)–Cu(1)–I(3) 113.64(8), I(1)–Cu(1)–I(1A) 106.36(7), I(2)–Cu(1)–I(1A) 103.52(7), I(3)–Cu(1)–I(1A) 111.54(8).

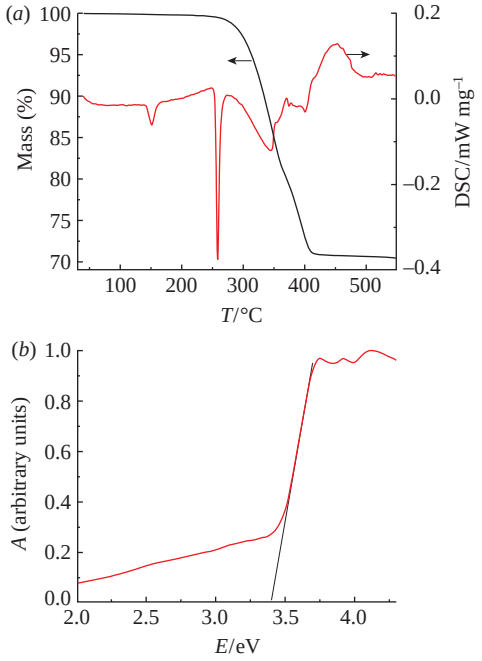


Figure 3 (*a*) STA and (*b*) absorption spectrum of $(MeNH_3)Cu_2I_3$.

Table 1 Intermolecular hydrogen bonds in $(MeNH_3)Cu_2I_3$.

N–H···I	*d*(N–H)/Å	*d*(H···I)/Å	*d*(N···I)/Å	∠(NHI)/deg
N(1)–H(1A)···I(3)	0.91	3.06	3.591(17)	119
N(1)–H(1B)···I(2)	0.91	2.82	3.713(8)	169

the same phase crystallized from a droplet in the case of the stoichiometric (1 : 1) ratio of $(MeNH_3)I$: CuI.

The target compound $(MeNH_3)Cu_2I_3$ crystallizes in a monoclinic unit cell. Its structure represents a salt containing infinite double-chained $\{[Cu_2I_3]^-\}_\infty$ anions and isolated $[MeNH_3]^+$ cations (Figure 2). In the crystal, both the cations and anions occupy special positions on mirror planes [the $C_s(m)$ intrinsic symmetry]. In the anions, the copper atoms adopt a distorted tetrahedral coordination with the Cu–I distances of 2.633(2)–2.722(2) Å and the I–Cu–I bond angles of 103.52(7)–113.93(8)°. The central iodine atoms linking the two chains of the anions have a tetragonal-pyramidal environment, and the peripheral iodine atoms are in an angular configuration. As expected, the bond lengths for the central four-coordinate iodine atoms [2.685(2)–2.722(2) Å] are larger than those for the two-coordinate peripheral iodine atoms [2.633(2)–2.636(2) Å]. The cations and anions in $(MeNH_3)Cu_2I_3$ are bound to each other *via* N–H···I hydrogen bonds (Table 1) into H-bonded ribbons propagating along the [010] direction (Figure 2).

Note that the double chained structure of the anions $Cu_2I_3^-$ in $(MeNH_3)Cu_2I_3$ is very similar to that in the related orthorhombic compounds $RbCu_2I_3$,[9] $CsCu_2I_3$[10] and $MePyCu_2I_3$,[14] while $(Me_4N)Cu_2I_3$ and $(Et_4N)Cu_2I_3$ with more well-screened cations are triclinic with single $Cu_2I_3^-$ chains.[12,13] However, the $\{Cu_2I_3\}_\infty$ chains within the anions of $(MeNH_3)Cu_2I_3$ are more tightly arranged [the interchain $(Cu\cdots Cu)_\perp$ distance is 3.013(4) Å] than those within the anions of $RbCu_2I_3$ [the interchain $(Cu\cdots Cu)_\perp$ distance is 3.425(6) Å], while the $(Cu\cdots Cu)_{||}$ distances within the chains are very close to each other [2.886(4) and 2.864(2) Å, respectively]. Contrary to $RbCu_2I_3$, the $\{Cu_2I_3\}_\infty$ chains within the anions of $CsCu_2I_3$ are stretched out in comparison with those in $(MeNH_3)Cu_2I_3$ [the $(Cu\cdots Cu)_{||}$ distance in $CsCu_2I_3$ is 3.036(3) Å], while the interchain $(Cu\cdots Cu)_\perp$ distances are very close to each other [in $CsCu_2I_3$ it is 3.131(4) Å]. Moreover, the $\{Cu_2I_3\}_\infty$ chains within the anions of $MePyCu_2I_3$ are even more stretched out in comparison with those in $(MeNH_3)Cu_2I_3$ and $CsCu_2I_3$ [the $(Cu\cdots Cu)_{||}$ distance in $MePyCu_2I_3$ is 3.144(2) Å], though the interchain $(Cu\cdots Cu)_\perp$ distance of 2.947(4) Å remains nearly equal.

The most related compounds, $RbCu_2I_3$ and $CsCu_2I_3$, are semiconductors with band gaps of 4.02 and 3.89 eV, respectively.[19] To frame a range of hypothetical practical applications of the new compound, we estimated its band gap energy and evaluated its thermal stability. The thermal analysis revealed that the obtained phase is stable up to 260 °C, and it undergoes two phase transitions at 140 and 250 °C [Figure 3(*a*)]. The former is not accompanied by weight loss, while the latter is melting followed by decomposition. During this process, the weight loss of ~29.5% is observed, which corresponds to the elimination of $(MeNH_3)I$ leaving the pure CuI phase. The UV-VIS absorption spectrum of $(MeNH_3)Cu_2I_3$ [Figure 3(*b*)] reveals an absorption edge at ~3.40 eV, which is smaller than that of $RbCu_2I_3$ and $CsCu_2I_3$; thus, the new compound is of interest for potential optical applications.

In conclusion, a new hybrid semiconductor with a band gap of ~3.4 eV, namely, $(MeNH_3)Cu_2I_3$ was obtained. Two synthesis approaches were found to result in pure $(MeNH_3)Cu_2I_3$: the crystallization of a solution of CuI and $(MeNH_3)I$ in acetonitrile and the grinding of the solid precursors in a mortar. The crystal structure of the compound is very similar to that of related compounds. Simultaneous thermal analysis showed that $(MeNH_3)Cu_2I_3$ is stable up to ~250 °C, and it undergoes a phase transition at 150 °C.

Radiation Source. In total, 480 frames were collected with an oscillation range of 1.0° in the φ scanning mode using two different orientations of the crystal. The semi-empirical correction for absorption was applied using the Scala program.[20] The data were indexed and integrated using the utility iMOSFLM from the CCP4 software suite.[21,22] The structure was solved by intrinsic phasing modification of direct methods[23] and refined by a full-matrix least-squares technique on F2 with anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were localized in the difference-Fourier maps and refined within the riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(N,C)]. All calculations were carried out using the SHELXTL program suit.[24]

CCDC 1590175 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

This study was supported by the Russian Ministry of Education and Science (grant no. 14.607.21.0147; RFMEFI60716X0147).

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Received: 19th December 2017; Com. 17/5437